

RAOULT'S LAW

Foundation of Chem II
Chemistry for Pet Eng II

Raul's Law

- *The vapour pressure of a solution of a non-volatile solute is equal to the vapour pressure of the pure solvent at that temperature multiplied by its mole fraction.*

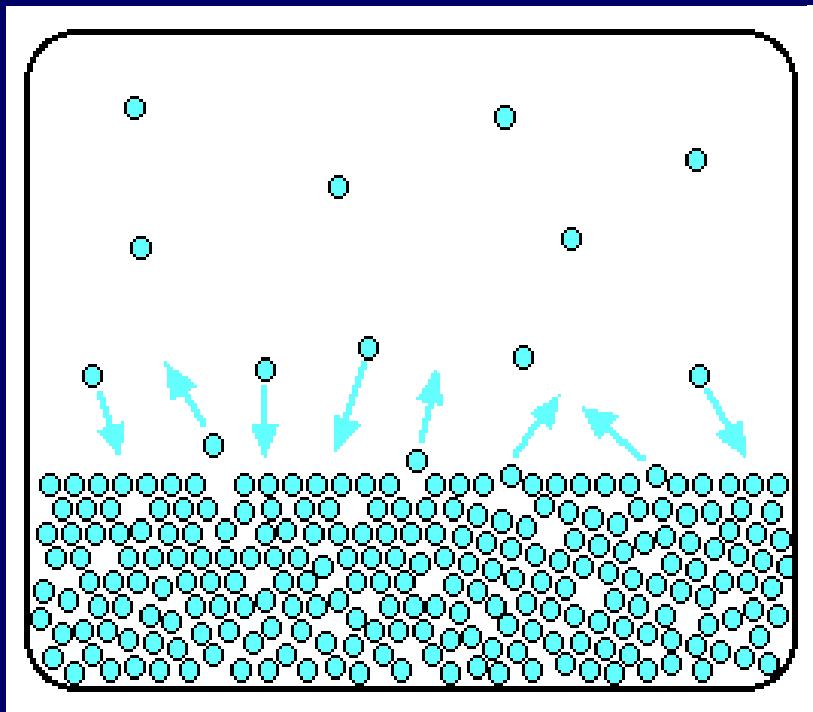
Limitation of Raoult's law: It applies to IDEAL SOLUTIONS. This why R-L is defines as any solution which obey's Raoult's law

$$P = x_{\text{solvent}} \times P^{\circ}_{\text{solvent}}$$

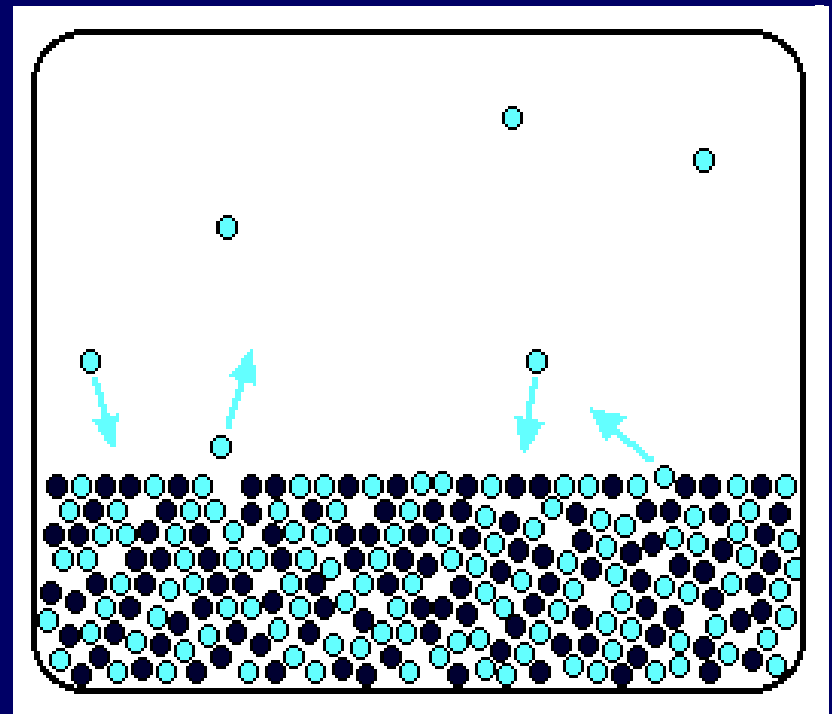
P° = the vapour of the pure solvent

x_{solvent} = mole fraction of the solvent

$$x_{\text{solvent}} = \frac{\text{moles of solvent}}{\text{total number of moles}}$$



Pure solvent
surface
occupied by solute particles

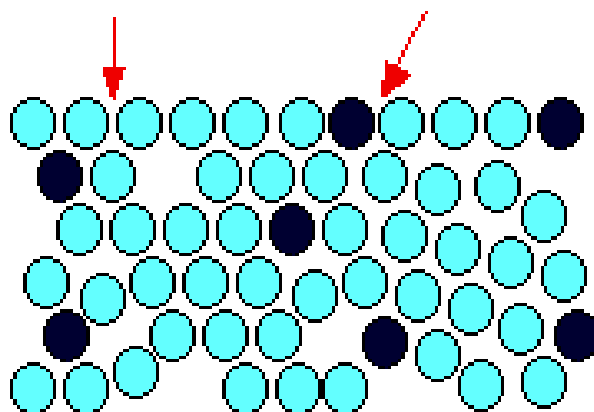


solution with 50% of the
sites

Features of an ideal solution

In an ideal solution, the forces between the solvent molecules ...

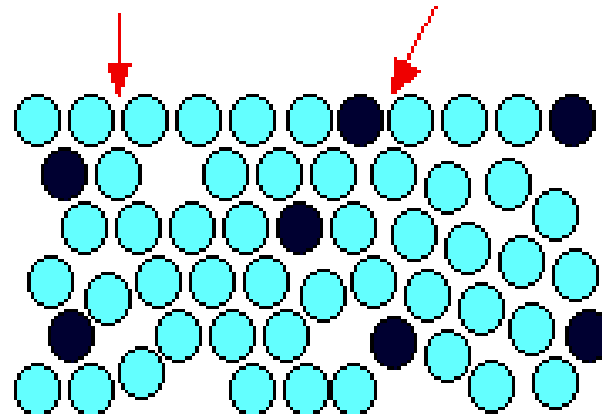
... are exactly the same as those between solvent and solute.



That means that it takes the same amount of energy for solvent molecules to break away from the surface in either case.

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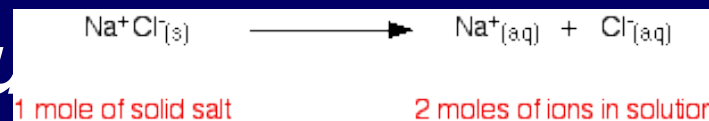
. . . are exactly the same as those between solvent and solute.



That means that it takes the same amount of energy for solvent molecules to break away from the surface in either case.

- In any real solution of, say, a salt in water, there *are* strong attractions between the water molecules and the ions. That would tend to slow down the loss of water molecules from the surface. However, if the solution is sufficiently dilute, there will be good-sized regions on the surface where you still have water molecules on their own. The solution will then approach ideal behaviour

The nature of the solution

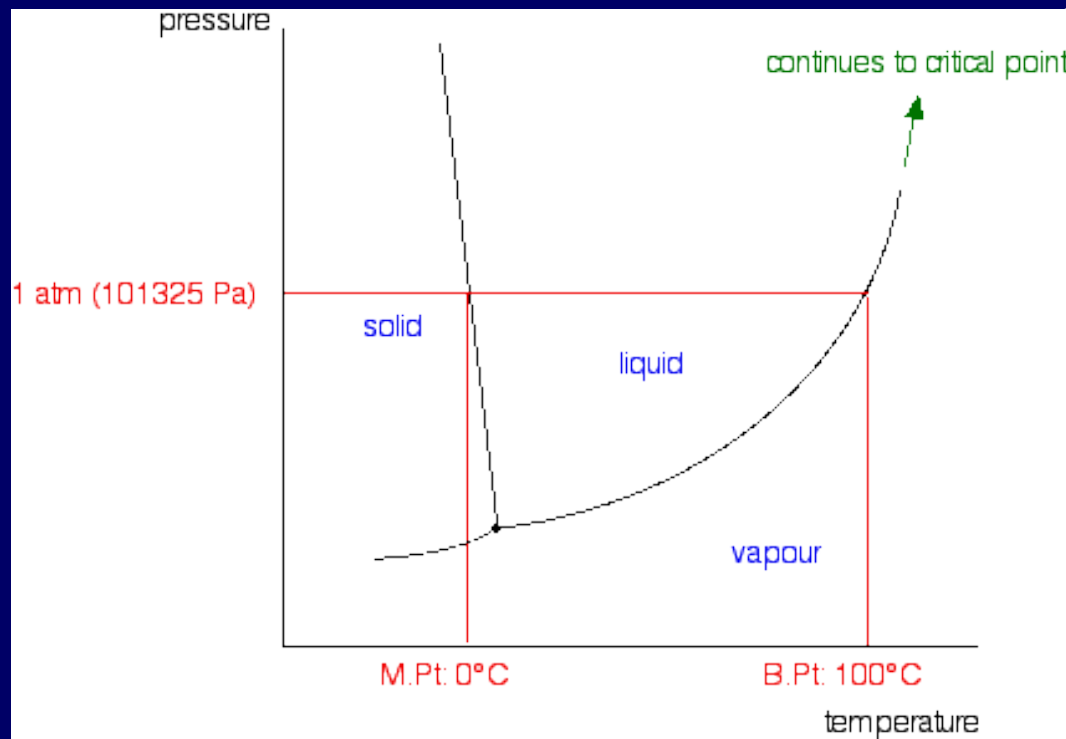


- What matters isn't actually the number of moles of substance that you put into the solution, but the number of moles of particles **formed**. For each mole of sodium chloride dissolved, you get 1 mole of sodium ions and 1 mole of chloride ions - in other words, you get twice the number of moles of particles as of original salt.
- So, if you added 0.1 moles of sodium chloride, there would actually be 0.2 moles of particles in the solution - and that's the figure you would have to use in the mole fraction calculation.

- Unless you think carefully about it, Raoult's Law only works for solutes which don't change their nature when they dissolve. For example, they mustn't ionise or associate (in other words, if you put in substance A, it mustn't form A_2 in solution).

Raoult's Law and melting and boiling points

- The effect of Raoult's Law is that the saturated vapour pressure of a solution is going to be lower than that of the pure solvent at any particular temperature. That has important effects on the phase diagram of the solvent.
- The next diagram shows the phase diagram for pure water in the region around its normal melting and boiling points. The 1 atmosphere line shows the conditions for measuring the normal melting and boiling points.

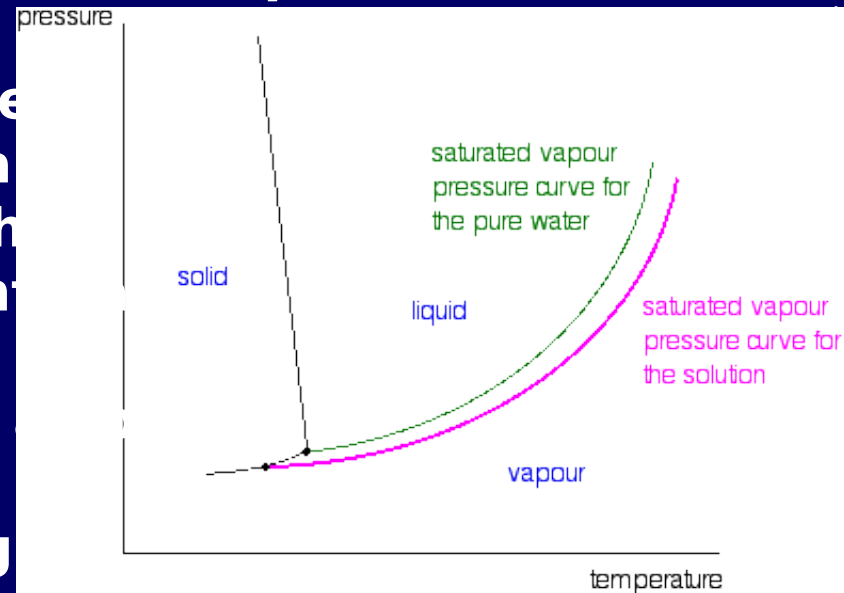


The line separating the liquid and vapour regions is the set of conditions where liquid and vapour are in equilibrium. It can be thought of as the effect of pressure on the boiling point of the water, but it is also the curve showing the effect of temperature on the saturated vapour pressure of the water. These two ways of looking at the same line were discussed briefly in the phase diagrams

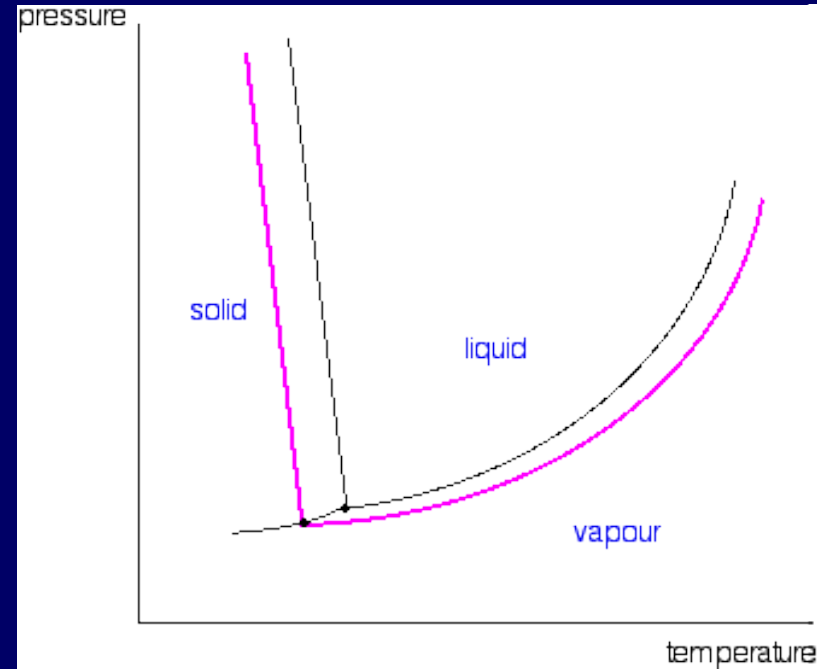
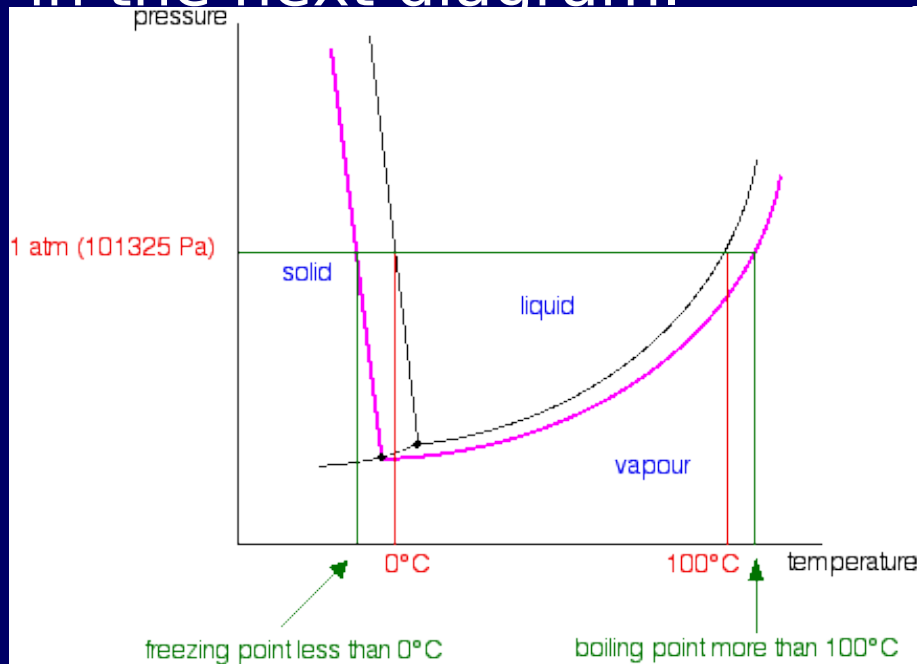
If you draw the saturated vapour pressure curve for a solution of a non-volatile solute in water, it will always be lower than the curve for the pure water.

If you look closely at the last diagram, you will see that the point at which the liquid-vapour equilibrium curve meets the solid-vapour curve has moved. That point is the triple point of the system - a unique set of temperature and pressure

conditions at which it is possible to get solid, liquid and vapour at equilibrium with each other at the same time. Since the triple point solid-liquid equilibrium is present (amongst other equilibria), it is a melting point of the system - although not *the normal* melting point because the pressure isn't 1 atmosphere.



This means that the phase diagram needs a new melting point line (a solid-liquid equilibrium line) passing through the new triple point. That is shown in the next diagram.



Because of the changes to the phase diagram, you can see that:

- 1. the boiling point of the solvent in a solution is higher than that of the pure solvent;**
- 2. the freezing point (melting point) of the solvent in a solution is lower than that of the pure solvent.**

- Remember that the previous case represents $C=2$ only . The same is true for many components systems e.g. water containing ethanol and acetone ...etc.

RAOULT'S LAW AND IDEAL MIXTURES OF LIQUIDS

- We shall discuss how Raoult's Law applies to mixtures of two volatile liquids. We shall covers cases where the two liquids are *entirely miscible* in all proportions to give a single liquid
- An ideal mixture is one which obeys Raoult's Law,
- We shall examine the characteristics of an ideal mixture before actually stating Raoult's Law

Examples of ideal mixtures

- There is actually no such thing as an ideal mixture! However, some liquid mixtures get fairly close to being ideal. These are mixtures of two **very closely** similar substances.

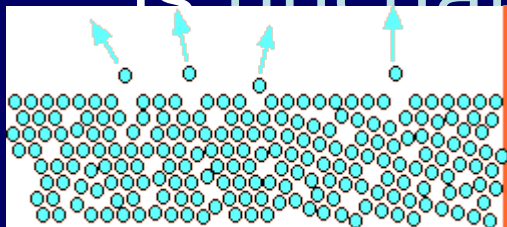
Commonly quoted examples include:

- hexane and heptane
- benzene and methylbenzene
- propan-1-ol and propan-2-ol

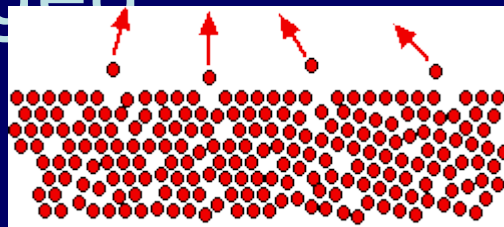
Ideal mixtures and intermolecular forces

- In a pure liquid, some of the more energetic molecules have enough energy to overcome the intermolecular attractions and escape from the surface to form a vapour.
- The smaller the intermolecular forces, the more molecules will be able to escape at any particular temperature.
- If you have a second liquid, the same thing is true. At any particular temperature a certain proportion of the molecules will have enough energy to leave the surface.

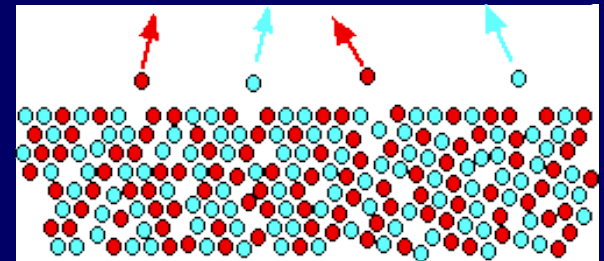
- In an ideal mixture of these two liquids, the tendency of the two different sorts of molecules to escape is unchanged



Liquid 1



Liquid 2



50:50

Mixture of 1+2

You might think that the diagram shows only half as many of each molecule escaping - but the *proportion* of each escaping is still the same. The diagram is for a 50/50 mixture of the two liquids. That means that there are only half as many of each sort of molecule on the surface as in the pure liquids. If the *proportion* of each escaping stays the same, obviously only half as many will escape in any given time.

- If the red molecules still have the same tendency to escape as before, that must mean that the intermolecular forces between two red molecules must be exactly the same as the intermolecular forces between a red and a blue molecule.
- If the forces were any different, the tendency to escape would change.
- Exactly the same thing is true of the forces between two blue molecules and the forces between a blue and a red. They must also be the same otherwise the blue ones would have a different tendency to escape than before.
- *If you follow the logic of this through, the intermolecular attractions between two red molecules, two blue molecules or a red and a blue molecule must all be exactly the same if the mixture is to be ideal.*

- This is why mixtures like hexane and heptane get close to ideal behaviour. They are similarly sized molecules and so have similarly sized van der Waals attractions between them. However, they obviously aren't identical - and so although they get close to being ideal, they aren't actually ideal
- **Ideal mixtures and enthalpy change of mixing**
- When you make any mixture of liquids, you have to break the existing intermolecular attractions (which needs energy), and then remake new ones (which releases energy).
- If all these attractions are the same, there won't be any heat either evolved or absorbed.
- That means that an ideal mixture of two liquids will have ***zero enthalpy change of mixing***. If the temperature rises or falls when you mix the two liquids, then the mixture isn't ideal.

Application of Raoult's Law

- ***R-L states that:***
- ***The partial vapour pressure of a component in a mixture is equal to the vapour pressure of the pure component at that temperature multiplied by its mole fraction in the mixture.***
- ***Raoult's Law only works for ideal mixtures***

- In equation form, for a mixture of liquids A and B, this reads:

$$p_A = x_A \times P_A^{\circ}$$

$$p_B = x_B \times P_B^{\circ}$$

- In this equation, p_A and p_B are the partial vapour pressures of the components A and B. In any mixture of gases, each gas exerts its own pressure. This is called its partial pressure and is independent of the other gases present. Even if you took all the other gases away, the remaining gas would still be exerting its own partial pressure.
- The total vapour pressure of the mixture is equal to the sum of the individual partial pressures.

$$\text{Total vapour pressure} = p_A + p_B$$

- The P_o values are the vapour pressures of A and B if they were on their own as pure liquids.
- x_A and x_B are the mole fractions of A and B. That is exactly what it says it is - the fraction of the total number of moles present which is A or B.
- You calculate mole fraction using, for example:

$$x_A = \frac{\text{moles of A}}{\text{total number of moles}}$$

- Example: Suppose you had a mixture of 2 moles of methanol and 1 mole of ethanol at a particular temperature. The vapour pressure of pure methanol at this temperature is 81 kPa, and the vapour pressure of pure ethanol is 45 kPa.
- There are 3 moles in the mixture in total.
- 2 of these are methanol. The mole fraction of methanol is $\frac{2}{3}$.
- Similarly, the mole fraction of ethanol is $\frac{1}{3}$.
- You can easily find the partial vapour pressures using Raoult's Law - *assuming that a mixture of methanol and ethanol is ideal.*

For methanol	$p_{\text{methanol}} = \frac{2}{3} \times 81$	For ethanol	$p_{\text{ethanol}} = \frac{1}{3} \times 45$
=	= 54 kPa	=	= 15 kPa

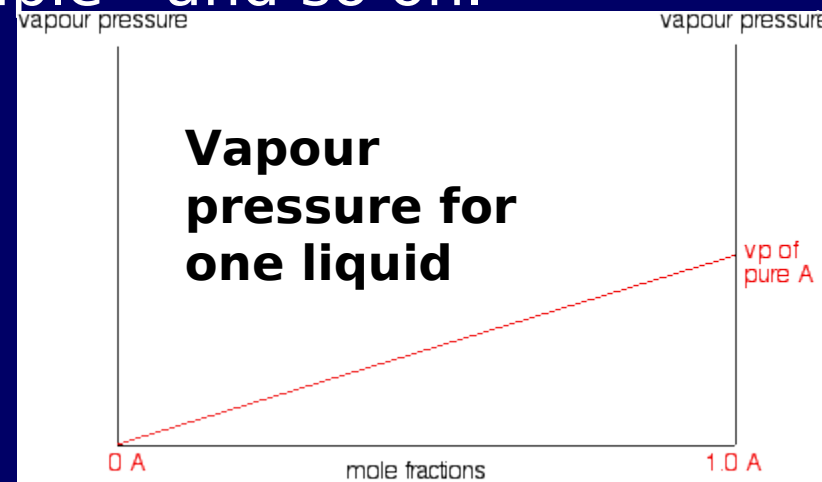
$$\text{Total vapour pressure} = 54 + 15$$

$$= 69 \text{ kPa}$$

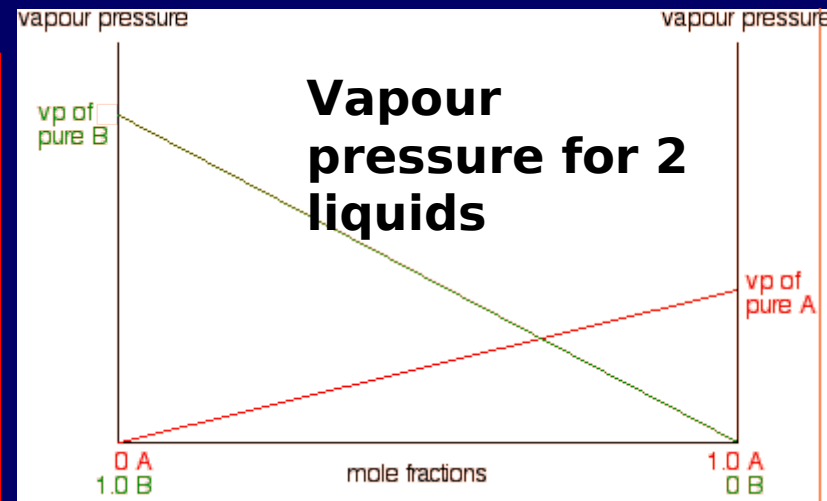
Vapour pressure / composition diagrams

- Suppose you have an ideal mixture of two liquids A and B. Each of A and B is making its own contribution to the overall vapour pressure of the mixture - as we've seen above.
- Let's focus on one of these liquids - A, for example.
- Suppose you double the mole fraction of A in the mixture (keeping the temperature constant). According to Raoult's Law, you will double its partial vapour pressure. If you triple the mole fraction, its partial vapour pressure will triple - and so on.

• In other words, the partial vapour pressure of A at a particular temperature is proportional to its mole fraction. If you plot a graph of the partial vapour pressure of A against its mole fraction, you will get a straight line.

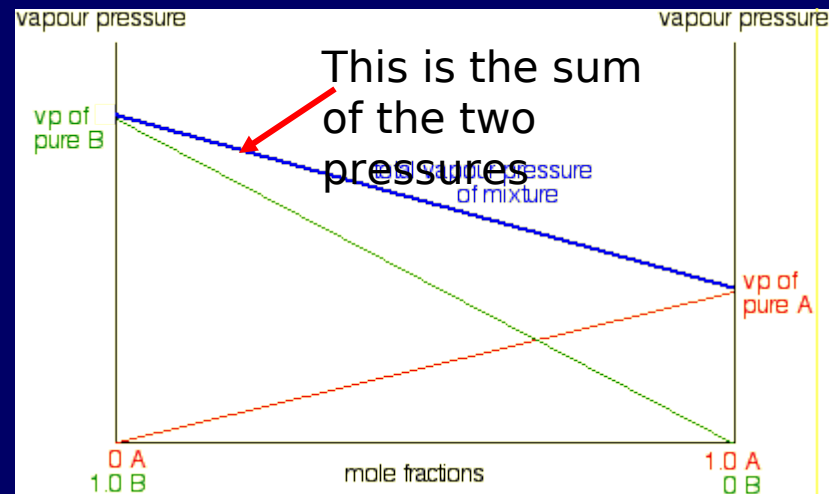


Now we'll do the same thing for B - except that we will plot it on the same set of axes. The mole fraction of B falls as A increases so the line will slope down rather than up. As the mole fraction of B falls, its vapour pressure will fall at the same rate



Notice that the vapour pressure of pure B is higher than that of pure A. That means that molecules must break away more easily from the surface of B than of A. B is the more volatile liquid.

To get the total vapour pressure of the mixture, you need to add the values for A and B together at each composition. The net effect of that is to give you a straight line as shown in the next diagram.



Boiling point / composition diagrams

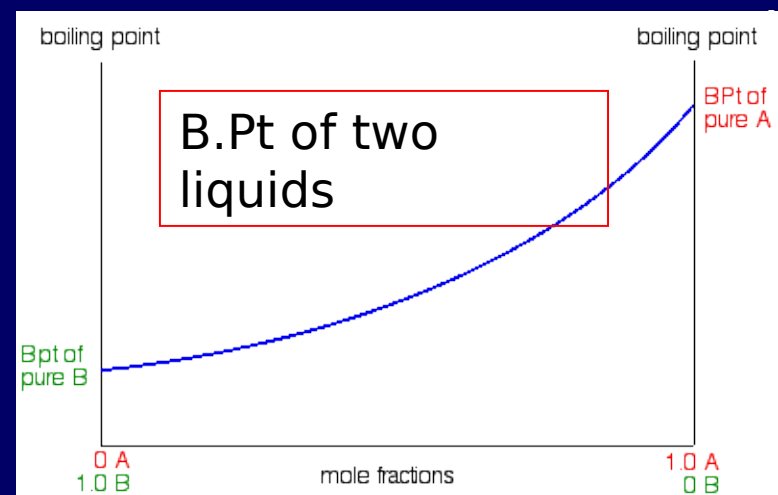
The relationship between boiling point and vapour pressure

- If a liquid has a high vapour pressure at a particular temperature, it means that its molecules are escaping easily from the surface.
- If, at the same temperature, a second liquid has a low vapour pressure, it means that its molecules aren't escaping so easily.
- What does that imply about the boiling points of the two liquids? There are two ways of looking at this:

- Either:
- If the molecules are escaping easily from the surface, it must mean that the intermolecular forces are relatively weak. That means that you won't have to supply so much heat to break them completely and boil the liquid.
- The liquid with the higher vapour pressure at a particular temperature is the one with the lower boiling point.
- Or:
- Liquids boil when their vapour pressure becomes equal to the external pressure. If a liquid has a high vapour pressure at some temperature, you won't have to increase the temperature very much until the vapour pressure reaches the external pressure. On the other hand if the vapour pressure is low, you will have to heat it up a lot more to reach the external pressure.

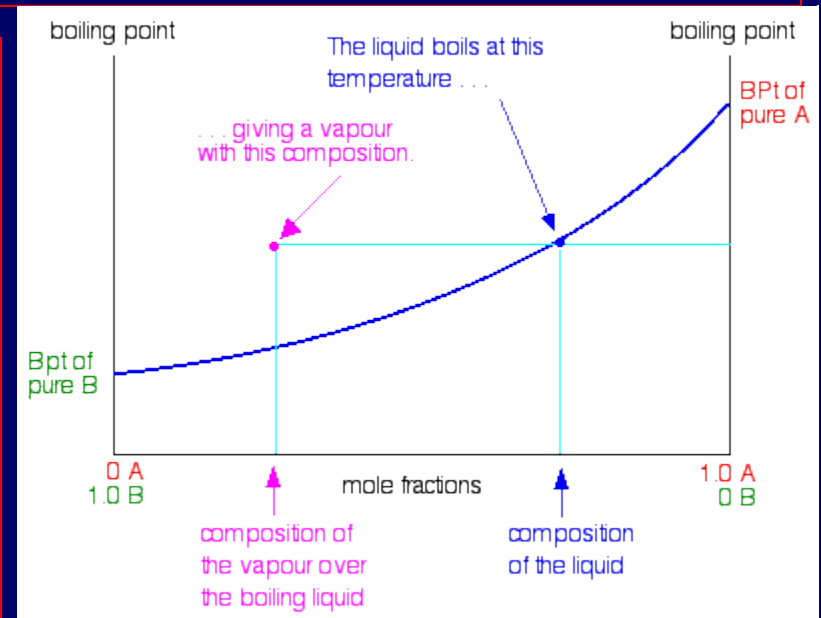
Constructing a boiling point / composition diagram

- We'll start with the boiling points of pure A and B.
- B has the higher vapour pressure. That means that it will have the lower boiling point.
- For mixtures of A and B, you might perhaps have expected that their boiling points would form a straight line joining the two points we've already got. Not so!
- In fact, it turns out to be a curve.

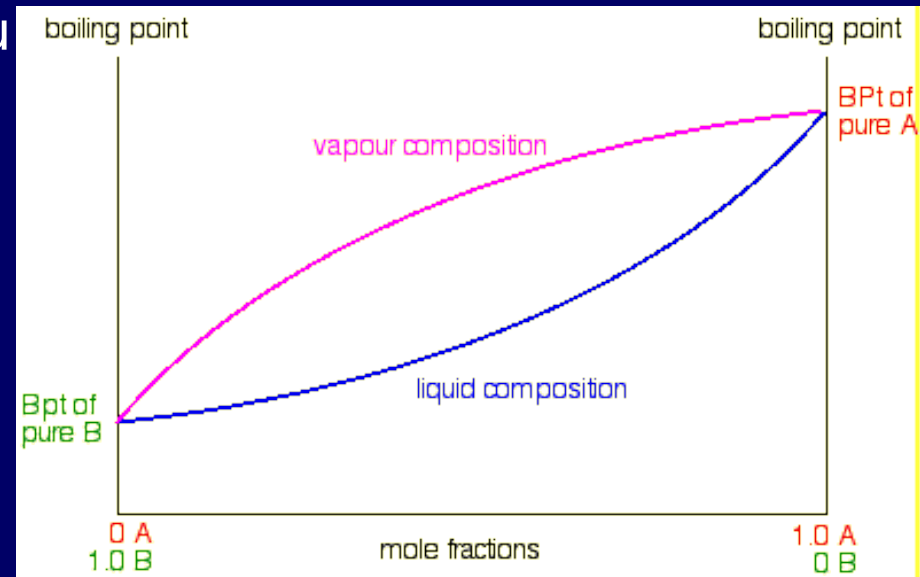
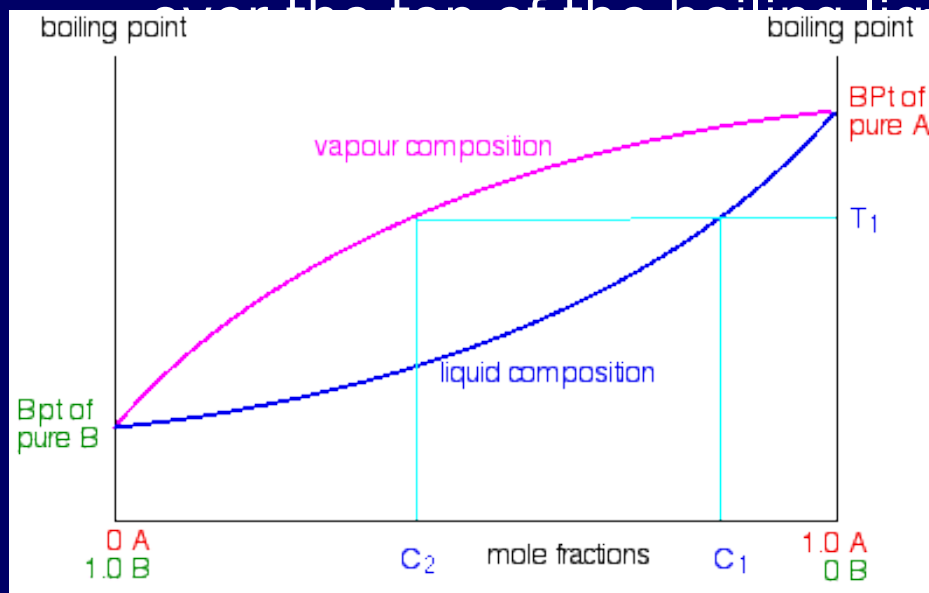


- If you boil a liquid mixture, you would expect to find that the more volatile substance escapes to form a vapour more easily than the less volatile one.
- That means that in the case we've been talking about, you would expect to find a higher proportion of B (the more volatile component) in the vapour than in the liquid. You can discover this composition by condensing the vapour and analysing it. That would give you a point on the diagram

The diagram just shows what happens if you boil a particular mixture of A and B. Notice that the vapour over the top of the boiling liquid has a composition which is much richer in B - the more volatile component. If you repeat this exercise with liquid mixtures of lots of different compositions, you can plot a second curve - a vapour composition line.



- **Using the phase diagram**
- The diagram is used in exactly the same way as it was built up. If you boil a liquid mixture, you can find out the temperature it boils at, and the composition of the vapour over the boiling liquid.
- For example, in the next diagram, if you boil a liquid mixture C1, it will boil at a temperature T1 and the vapour



This is how we arrive to the beginnings of fractional distillation